COATINGS

COATINGS FOR THERMO-REINFORCEMENT OF HEATPROOFING MATERIALS AND QUASIPLASTIC CERAMICS

S. S. Solntsev,[1] V. A. Rozenenkova,[1] and N. A. Mironova[1]

Thermo-reinforcing coatings based on ceramic-forming polymers and oxygen-free modifying refractory nanoparticles are investigated. It is established that thermo-reinforcing coatings increase the working temperatures of fibrous heat-insulating materials by 300 – 500°C and increase the thermal and mechanical properties by a factor two or three. A new multifunctional glass-ceramic composite thermo-reinforced material which can be used in heat-insulating, heat-proofing, and sound-absorbing structures in aerospace and power engineering has been developed.

The operational properties of heat-proof, heat-insulating, sound-absorbing, and building materials made of glass and other staple (short) and continuous inorganic fibers can be greatly increased if a special coating that modifies the surface of a fiber and simultaneously secures fibers at sites where they touch one another is deposited on the fiber surfaces. Such coatings are said to be "thermo-reinforcing" coatings (TRCs), because they effectively act on the mechanical properties of fibrous materials under thermal loads. The use of these coatings can be viewed as a method for increasing the thermal and mechanical properties of fibrous heat-shielding and building materials [1].

The objective of our work is to develop ceramic thermo-reinforcing coatings based on organoelemental ceramic-forming polymers and nanodispersed refractory modifying additives and materials with such coatings.

The thermo-reinforcing coatings were synthesized on the basis of silicon dioxide, carbide, and nitride. TRCs with a complex composition were obtained by pyrolytic decomposition of polysilazanes, polycarbosilanes, and polyboroethoxysiloxanes with additives consisting of thermodynamically stable refractory nanodispersed oxygen and oxygen-free compounds [2].[2]

A characteristic feature of the technological process in which inorganic polymers are used to produce thermo-reinforced coatings is solid-phase synthesis of a specified ceramic layer on fiber surfaces throughout the entire volume of the materials [3].

Ultrathin alumina, quartz, carbon, and silicon carbide fibers in the form of fabrics and preformed mats were used as the base for obtaining a strengthened heatproofing material. The samples of quartz fibers had a low density ($120 – 800 \, kg/m^3$), low thermal conductivity ($0.06 \, W/(m \cdot K)$ at 20°C and $0.25 \, W/(m \cdot K)$ at 1200°C), and resistance to chemical and biological attack, which is important for aerospace engineering. The coatings were deposited on a fiberglass material by vacuum and free permeation. The effect of the sequence of permeations by solutions with different concentrations was investigated in order to achieve the maximum content of the ceramic-forming polymer and a uniform distribution of this polymer over the volume of the microporous glass-fiber material.

The density of the samples after five permeation cycles is four times higher than that of the initial samples. It was found that as the concentration of the working solutions increases and the solutions are modified, the density of the samples increases as the concentration of the solutions of the binding agents and the growth of the density slows down proportionately as the number of permeation cycles increases. The maximum density of the samples was $300 – 500 \, kg/m^3$.

The formation of TRCs proceeds in the following stages: low-temperature gel formation, low-temperature solidification, and high-temperature solidification. After solidification the samples were subjected to pyrolysis. The coating was formed in an inert medium and in air at atmospheric pressure. The yield of the pyrolytic residue was 83 – 89%.

---

[1] Federal State Unified Enterprise "All-Russia Scientific-Research Institute for Aviation Materials," Moscow, Russia.
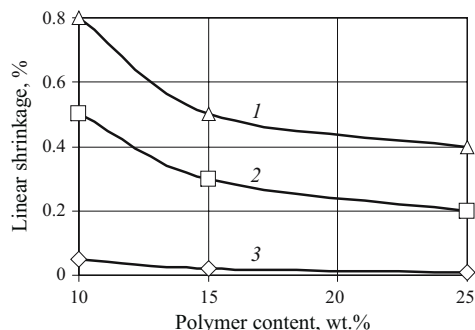[2] N. I. Shvets, S. V. Gavrilov, and V. G. Lepshchikov participated in this work.

Fig. 1. Temperature stability of HPM as a function of the TRC composition at 750°C with holding time 750 h. Curves *1*, *2*, *3*) 0.1, 0.3, and 0.5 wt.%, respectively, of the modifying additive.

The formation temperature of the coating was reduced by 300 – 500°C to prevent undesirable phase transformations in the material. X-ray phase analysis shows that the amorphous phases of SiO_2, SiC, Si_3N_4, and $SiOB$ were present and cristobalite was absent. Electron microscopy established that the ceramic layer is a nanostructural gradient coating with a scaly structure.

The temperature stability of the heatproofing material (HPM) was investigated as a function of the TRC (Fig. 1).

Analysis of the data obtained showed that all HPMs samples with TRCs are temperature-stable up to 750°C with holding times up to 750 h. The linear shrinkage of the samples after the tests was less than 1%. As the amount of ceramic-forming polymer increases to 25% and the content of the modifying nanodispersed additive to 0.5%, the linear shrinkage decreases by a factor of 8 – 10. The change in the lineal dimensions of the samples — not more than 0.1% — shows that the compositions synthesized are optimal.

x-ray phase analysis confirms that the HPMs with a TRC are temperature-stable. The phase composition of the initial HPM samples with TRCs and samples which were tested for temperature stability and thermal shock resistance following a regime with temperature 750°C and test duration 750 h was studied. All samples were investigated using a Rigaku D/MAX-2500 diffractometer. The diffraction patterns of all samples were identical — the samples are amorphous, indicating that the material is phase-stable.

The temperature stability and thermal shock resistance of the HPM samples with and without a TRC were investigated at 750°C with holding time 750 h and 1000 – 1500°C with holding time 2 h. The tests were performed in a high-temperature furnace with periodic measurement of the linear dimensions of the samples after a 150 h holding period at 750°C and a 2 h holding period at 1000 – 1500°C. The thermal shock resistance tests were performed on samples with and without a coating following the regime $20 \rightarrow 750 \rightarrow 20$°C; the holding time at 750°C was 1 h. The criterion for judging the thermal shock resistance of the samples was the number of thermal cycles up to the formation of the first defect. The results of the tests are presented in Fig. 2.
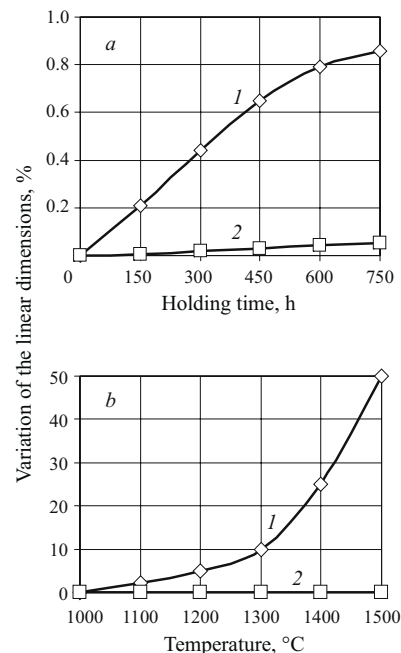

Fig. 2. Shrinkage of the samples versus the holding time at 750°C (*a*) and versus the temperature with holding time 2 h (*b*): *1*) uncoated HPM; *2*) coated HPM.
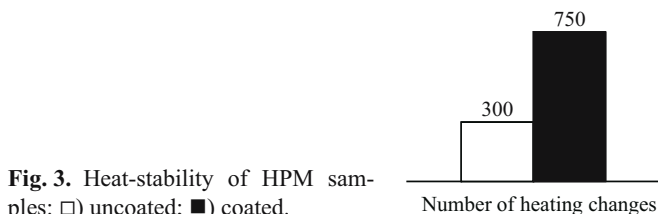

Fig. 3. Heat-stability of HPM samples: □) uncoated; ■) coated.

Figure 3 shows the results of the thermal shock resistance tests performed on HPM. The external appearance of the samples after the tests is shown in Fig. 4.

Cracks appeared in the uncoated HPM samples after 300 thermal cycles. The tests on the coated samples were terminated after 750 thermal cycles without any indications of damage. The TRCs made it possible to increase the thermal shock resistance of heat-proofing materials based on glass and quartz fibers by a factor of 2.5.

It was established that HPMs with TRCs are temperature-stable at temperatures up to 750°C for 750 h and at 1500°C for 2 h. The linear dimensions of samples with a three-layer coating did not change and no defects were observed on the surfaces of the samples.

Samples of HPM with TRC were prepared to perform mechanical tests at normal temperature (20°C) for bending and compression. Samples of fiberglass material were subjected to single, double, and triple permeations with a solution of PKS-M polycarbosilane with a modifying HD additive. The density of HPM samples with TRC was 180 – 200 kg/m³. Figure 5 shows the effect of the permeation cycles on the mechanical properties of HPM with TRC. Evidently, as the number of permeation cycles increases to four,
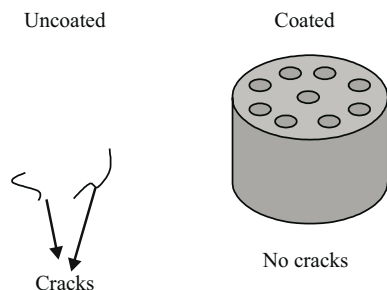
Uncoated   Coated

Cracks   No cracks

Fig. 4. HPM samples after tests for heat-stability.
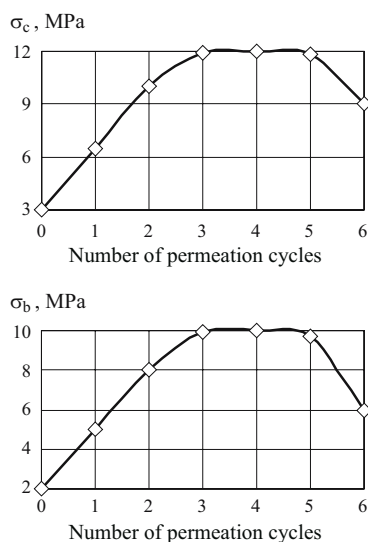
Fig. 5. Mechanical strength of HPM with TRC (at 20°C).

Fig. 6. Sample shrinkage versus holding time at 750°C: *1*) uncoated; *2*) unperforated HPM, TRC No. 1; *3*, *4*) perforated HPM, TRC Nos. 1 and 2, respectively.

the mechanical strength of the HPM samples with TRC increases by a factor 2 – 3 but after five permeation cycles the mechanical properties become sharply worse.

Special samples — 20 mm high and 30 mm in diameter — with density $0.16 – 0.20$ g/cm^3 were fabricated to investigate the acoustic properties of glass-fiber HPM with a ceramic TRC. Some of these samples were perforated to increase the porosity of the HPM. The samples had through openings 2 and 3 mm in diameter. The perforation area comprised 10, 15, and 20%. Samples with a homogeneous structure and perforation were pretested for the temperature stability at 750°C over 750 h.

The testing of samples of sound-absorbing structures based on HPM with TRC consisted of determining the sound absorption coefficient, which was determined in the frequency range $0.8 – 5.0$ kHz at sound pressure levels of approximately 140 dB on the surface of the sample at all frequencies.

Figure 6 shows that test results for HPM with TRC with different compositions. The sound absorption coefficient of the material studied remains virtually unchanged and high $(0.7 – 0.8)$ in a wide range of sound frequencies $(1.0 – 5.0$ kHz).

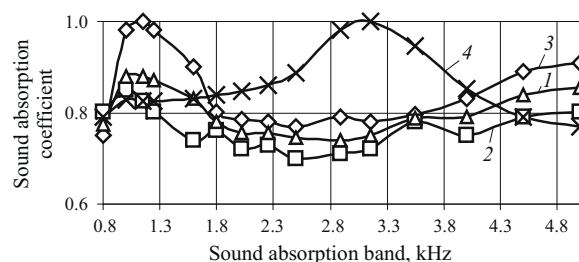HPM samples with TRC and combined perforations differing in shape and volume occupied in the material were investigated. The perforation volume ranged from 15 to 30%. It was found that as the perforated area of the samples increases to 30% the sound absorption coefficient increases to $0.9 – 1.0$ in the frequency range $1 – 3$ kHz.

Comprehensive tests showed that HPM with TRC could find application for development of sound-suppressing structures used in the airplane propulsion systems. The acoustic and mechanical properties of the heat-proofing and sound-suppressing materials which have been developed are determined by the morphology and perforation of the material and by the composition of and the technology used to form the TRC.

Coatings based on ceramic-forming polymers could find effective application for protecting quasiplastic glass-ceramic and ceramic composite materials. Reinforcing glass and ceramic matrices with carbon and silicon-carbide fibers (up to 50% fibers in the composite) makes it possible to obtain composites possessing quasiplasticity, i.e., the capability of withstanding dynamic and static loads without a monolithic part or sample being separated into several parts, as happens for ordinary glasses and ceramics. The quasiplasticity of these composites is due to the good resistance to crack growth and localization of the fracture stresses in the load application zone. Thermo-reinforcing coatings increase the crack resistance of structural reinforced ceramic composites and increase the reliability, thermal shock resistance, and oxidation resistance of carbon-containing materials.

The advantages of coatings of this type are primarily due to the possibility of controlling the material properties by selecting the appropriate initial components and determining their quantitative ratio, distribution, and orientation in the bulk of the composite material and by the coating technology.

REFERENCES

1. S. S. Solntsev, V. T. Minakov, V. A. Rozenenkova, et al., "Complex temperature-stable protective coatings for ceramic-ceramic composite materials," in: *Proceedings of the 18th Conference on Temperature-Stable Functional Coatings* [in Russian], Part 2, Izd. TGPU im. L. N. Tolstogo, Tula (2001), pp. 8 – 10.
2. S. S. Solntsev, V. T. Minakov, V. A. Rozenenkova, et al., "Thermo-reinforcing coatings for fibers of heat- and sound-absorbing materials," in: *Proceedings of the 19th All-Russia Conference on Temperature-Stable Functional Coatings* [in Russian], Vol. 2, YaNUS, St. Petersburg (2003), pp. 118 – 121.
3. S. S. Solntsev, *Protective Technological Coatings and Refractory Enamels* [in Russian], Mashinostroenie, Moscow (1984).